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SILICON REFINING METHOD AND INSTALLATION

The present invention relates to the manufacturing of silicon to form photovoltaic cells for electric power generation.

Silicon intended for photovoltaic techniques is presently essentially formed from the rejects of microelectronics industry, since the silicon used for photovoltaic applications can contain a proportion of impurities (on the order of 10^{-6}) that is less critical than the level of impurities (10^{-9}) generally required in microelectronics.

It would be desirable to have another silicon source to produce silicon adapted to photovoltaic products. In particular, the rejects of microelectronics industry risk becoming rapidly insufficient to satisfy the needs of photovoltaic techniques.

It is currently attempted to refine the silicon manufactured for metallurgic applications to obtain silicon having a purity adapted to photovoltaic techniques. The silicon used in metallurgy can contain several percents of impurities such as iron, titanium, boron, phosphorus, etc.

A method of silicon purification is known (for example, from European patent application 0,459,421), which consists of directing an arc plasma towards the surface of a silicon melt. The high speed of the plasma sets the melt in motion, the intensity of

which depends on the plasma power. The silicon is contained in a hot crucible with silica walls (SiO_2).

Such a method has several disadvantages. In particular, the use of an arc plasma requires electrodes that are a source of contamination for the silicon to be purified. Further, the oxygen in the silica wall is a source of contamination for the melt silicon.

The present invention aims at providing a novel method of silicon refining enabling reaching a high degree of purity, which is particularly well adapted to the refining of large quantities of silicon, and thus adapted to an industrial method for making silicon having a sufficient degree of purity for photovoltaic techniques.

The present invention aims, in particular, at overcoming the disadvantages of known methods.

The present invention also aims at providing a refining method that can be implemented from beginning to end in a same refining installation. In particular, the present invention aims at minimizing the use of refining means that are mechanically different from one another and at eliminating impurities of different natures within a same equipment.

The present invention further aims at having this same equipment usable to "dope" the silicon once refined.

To achieve these objects, the present invention provides a silicon refining method consisting of filling a cold inductive crucible with solid silicon; melting the content of the crucible; providing by means of the inductive crucible, a turbulent stirring of the silicon melt by bringing the liquid from the bottom of the crucible to the free surface by ascending along the central axis of the crucible; and directing a plasma generated by an inductive plasma torch towards the melt surface for a duration enabling the elimination of impurities for which the reactive gas of the plasma is adapted.

According to an embodiment of the present invention, the intensity of the turbulent stirring is a function of the frequency of an electromagnetic field created by the crucible.

According to an embodiment of the present invention, the method consists of sequentially using several reactive gases.

According to an embodiment of the present invention, the reactive gases are selected from the group including chlorine, oxygen, hydrogen, and water vapor.

According to an embodiment of the present invention, the method further consists of, after purification of the silicon melt, inverting the melt stirring direction and injecting, as a reactive gas of the plasma, a silicon doping element.

According to an embodiment of the present invention, the reactive gas injected to dope the silicon is hydrogen.

According to an embodiment of the present invention, the silicon is processed by batches of a volume substantially corresponding to the volume that can be contained in the crucible, the crucible not being integrally emptied at the end of the processing of a current batch to form a liquid seed furthering the melting during the next batch.

According to an embodiment of the present invention, during an initial starting phase of the installation, the plasma is used without any reactive gas to heat up the surface of the silicon load contained in the crucible, until this load reaches a temperature sufficient to make it conductive, the continuation of the load heating and its maintaining at the desired temperature being afterwards ensured by the magnetic field of the inductive crucible.

The present invention further provides a silicon refining installation including a cold inductive crucible adapted to receiving the silicon, an inductive plasma torch directed towards the free surface of the silicon load contained in the crucible, and a removable magnetic yoke between the plasma torch and the crucible, the yoke being ring-shaped to enable the passing of the plasma flame.

According to an embodiment of the present invention, the crucible includes, at its bottom, an aperture having its opening controlled by an electromagnetic valve.

The foregoing objects, features and advantages of the present invention will be discussed in detail in the following non-limiting description of specific embodiments in connection with the accompanying drawings, wherein:

Fig. 1 very schematically shows a refining installation according to the present invention during a silicon purification phase; and

Fig. 2 shows the installation of Fig. 1 during a silicon doping phase according to the present invention.

The same elements have been designated by the same reference in the different drawings. For clarity, only those elements of the installation that are necessary to the understanding of the present invention have been shown in the drawings and will be described hereafter.

According to the present invention, a silicon refining installation essentially includes a cold crucible 1 heated by induction (coil 12), intended for containing a silicon melt b, and an inductive plasma torch 2 directed for "flame" f to sweep the free surface of melt b.

The function of the plasma is to create a plasma medium formed of the free radicals and of the ions of the plasmid gas(es) in the vicinity of the free surface of silicon melt b. The atmosphere thus created at the free surface of the melt is extremely reactive and the impurities present at the melt surface combine with the reactive gas of the plasma and become volatile (or, conversely, solid) at the melt surface temperature. The entire installation is maintained under a controlled atmosphere, which enables evacuating the volatile molecules containing impurities as the process goes along.

The choice of an inductive plasma torch has, in particular as compared to the use of a plasma arc torch, the advantage of not contaminating the melt by the consumption of the electrode necessary to generate the plasma.

Another advantage of the use of a plasma torch, as compared to the use of an electron beam to focus significant power densities favorable to the direct vaporizing of the species at the

surface of a melt, is that, in the case of an inductive plasma, a system close to equilibrium is obtained, and advantage can thus be taken of the volatility differences between the elements or the compounds thereof. For example, the silicon can avoid being vaporized.

Another advantage is that the chemical action of the plasma at the liquid-plasma interface is distributed over the entire melt surface due to the plasma gas flow provided by the torch.

The use of a cold inductive crucible has several purposes. First, this has the advantage of not contaminating the liquid silicon, which is maintained in a skull, that is, a solid silicon skin (not shown) coats the inside of the crucible and contains the liquid silicon. Thus, the liquid silicon does not risk being contaminated by the material constitutive of walls 11 of the actual crucible, or of an intermediary wall as in known methods.

Another advantage of using a cold inductive crucible is that this enables creating a turbulent stirring in the silicon melt to further the purification. Indeed, in the absence of any stirring of the silicon melt, the diffusion times of the impurities that must migrate from the inside of the melted mass to the liquid-plasma interface to be combined, then vaporized, are incompatible with a method economically viable from an industrial point of view.

A feature of the present invention is that the magnetic field of the cold inductive crucible is, preferably, an A.C. single-phase field, that is, coil 12 of cold crucible 1 is supplied by an A.C. single-phase voltage. The choice of such a magnetic field has the advantage of causing the heating up of the silicon melt at the same time as it causes its motion.

Indeed, by submitting the silicon to an A.C. magnetic field by means of coil 12 of the crucible, flow variations are caused in the silicon that result in inducted currents located at the periphery of the material (in the electromagnetic skin).

The induced currents have thermal effects enabling heating (and thus melting) of the material, and mechanical effects (magnetic pressure and turbulent stirring) resulting from the

interaction between the currents and the applied magnetic field. When the material becomes liquid, the non-rotational part of the forces induces a magnetic pressure in the material, the free surface of which then becomes dome-shaped (Fig. 1). The rotational part of the forces induces driving torques within the liquid and sets it in motion in an electromagnetic stirring. This stirring is said to be turbulent since it causes not only high speed large scale recirculation (at the melt scale) to constantly and rapidly renew the free surface of the melt and bring the free species to be eliminated near the reactive surface, but also a small scale turbulence in the vicinity of the free surface to bring all the substances to be eliminated to the surface and thus increase reactional kinetics. All stirring scales are directly submitted to an injection of kinetic energy from the magnetic energy.

Conversely, a flow by hydraulic friction as used in known methods (EP-A-0,459,421) creates a large scale stirring and the motion is only transmitted by degradation and power transfer to smaller scales. In addition to the disadvantage of a large power loss to achieve small scale turbulence, such a method does not enable controlling the motion otherwise than by acting upon the arc plasma generating the motion.

According to the present invention, the selection of the frequency of the A.C. magnetic field enables setting the parameters (thermal effect, magnetic pressure, electromagnetic stirring) of the melt and, in particular, favoring one of the parameters.

According to the present invention, the frequency of coil 12 of crucible 1, powered by a generator 13, is chosen to further a turbulent stirring of silicon melt b that, in purification steps of the method of the present invention, is performed in the direction symbolized by the arrows in Fig. 1, that is, the liquid is brought from the bottom of the crucible to the free surface by ascending along the axis, the descent to the crucible bottom occurring at the periphery thereof.

Whether the stirring is turbulent or not depends on the current frequency, on the crucible size, and on the typical value of the magnetic field. The Reynolds number (Re) enables determining

the nature of the flow. The screen parameter ($R\omega$) is a function of the crucible diameter, of the electric conductivity of the melt, and of the frequency ($R\omega = \mu\sigma R^2$, where μ designates the permeability of vacuum,. ω designates the pulse, σ designates the electric conductivity of the liquid material, and R designates the crucible radius). The screen parameter characterizes the larger or smaller penetration of the field into the melt. If the field only very superficially penetrates (high frequencies), the Laplace forces will only act upon the peripheral portion of the melt and the stirring will be reduced. Similarly, if the field totally penetrates (zero frequency), there will be no stirring. For the stirring to be maximum, the screen parameter must have a value on the order of 40. It should be noted that this screen parameter is adjustable by the operator.

Such a stirring has several advantages in purification phases.

First, the fluid of the lower part of the crucible is rapidly brought up to the free reactive surface and the impurities can then be combined, then vaporized by the plasma to be evacuated. It should be noted that the species formed by reaction of the plasma with the impurities contained in the silicon are continuously eliminated in the installation and, accordingly, the interface reactivity is constant and does not saturate.

Another advantage of the circulation provided in Fig. 1 is that if solid particles (often lighter oxides), also resulting from the chemical reaction of impurities with the plasma, form on the melt surface, said particles are driven towards wall 11 of crucible 1, that is, towards the solid silicon crust where they are trapped, thus increasing the purification efficiency.

The choice of the crucible coil supply frequencies depends on the size and shape of the crucible. For example, with a crucible having a diameter on the order of 60 cm that can contain a silicon load on the order of 200 kg, a frequency on the order of 50 or 60 Hz, and thus the frequency of the industrial electric system, may be used for the crucible coil.

An advantage of the present invention is that it is now possible to simultaneously or successively inject, with no other manipulation than the opening of gas supply valves (not shown), several reactive gases g_r into the plasma and to control the concentration thereof with respect to the plasmid gases. In a torch 2 such as illustrated in Fig. 1, reactive gas g_r is brought to the center of the torch, and an auxiliary gas g_a, for example, argon, is conveyed concentrically to the reactive gases. A plasma gas g_p, for example, also argon, is further conveyed concentrically to the auxiliary gas. An inductive coil 21 surrounds the free end of torch 2 to create the inductive plasma. The torch coil is generally driven by an A.C. current at a frequency on the order of one MHz by a generator 22.

According to the present invention, different reactive gases may be injected into the plasma, either simultaneously or successively, for their selective action upon undesirable elements. As an example of reactive gases, oxygen, hydrogen, chlorine, or water vapor can be mentioned. The gas selection is determined by the chemical and thermodynamic properties of the impurity to be eliminated. The use of chlorine in the plasma enables forming volatile chlorides with impurities such as boron, antimony, or arsenic, which are among the most frequent impurities in the case of silicon coming from microelectronics industry rejects. Silicon also combines with chlorine to form a volatile chloride. The evaporation of impurities is furthered by the controlling of the renewal of the atmosphere above the silicon melt (a lower vapor pressure for impurity chlorides makes them more volatile).

Oxygen enables eliminating carbon traces (silicon is obtained by the reduction of sand (silica) by carbon in an arc furnace). It should be noted that the injection of a reactive gas such as oxygen is perfectly controllable, conversely to an oxygen release by a silica wall as in known methods.

Oxygen, or more efficiently water vapor, or the oxygen-hydrogen combination, enables making boron volatile as $B_3H_3O_6$, which is gaseous.

Practically, for obvious security and saving reasons, water or oxygen are preferred each time this is possible.

Preferably, the refining installation further includes a removable magnetic yoke 3 (Fig. 2), the function of which is to invert the flow direction in the silicon melt. The stirring speed being proportional to the typical value of the magnetic field, the presence or not of the magnetic yoke enables modifying this field and provides the flow speed and the fact that it is or not turbulent, without having to modify the frequency, which would create serious technological and fundamental difficulties. The function of magnetic yoke 3 will be better understood hereafter.

The present invention will now be described in relation with a preferred example of implementation of the silicon refining method in an installation such as described hereabove.

To begin with, cold crucible 1 is filled with silicon powders, chips, or scraps coming, for example, from a container 4. Since silicon is a semiconductor, it must be preheated before becoming progressively conductive (around 800°C) and then being likely to be heated up by induction by means of coil 12 of crucible 1.

According to the present invention, plasma torch 2 is first operated to preheat the solid silicon load and bring it to the temperature enabling obtaining a coupling with the low frequency field created by coil 12 of crucible 1. The gas used in the preheating phase preferably is argon. Hydrogen may be introduced as a reactive gas to increase the thermal conductivity of the plasma and thus accelerate the preheating of the silicon load.

An advantage of performing a preheating by means of the plasma torch as compared to the conventional use of a susceptor is that any contamination of the silicon that would otherwise be brought by the susceptor material (generally carbon or iron) is thus avoided.

At the end of this starting phase, the silicon has entirely melted down and the power required to maintain this melted state is essentially provided by the coil of crucible 1.

In a second purification phase, a turbulent stirring of the silicon melt in the arrow direction in Fig. 1 is furthered, and one or several reactive gases adapted to eliminating impurities which, by combining with a reactive gas at the surface of melt b, form volatile species that are vaporized, are simultaneously or successively introduced into the plasma. It should be noted that the traces of oxygen (or of other impurities) contained in the powders and chips introduced by solid silicon dispenser 4 in the preceding step cause the forming of a gangue at the melt surface. This gangue, formed of oxides and suboxides lighter then the rest of the melt, is rejected at the periphery of crucible 1 by the turbulent stirring in the arrow direction in Fig. 1. A clear surface is thus guaranteed at the liquid-plasma interface.

The purification phase may include several steps corresponding to the use of different reactive gases depending on the elements to be eliminated from the liquid melt.

Another feature of the present invention applied to the obtaining of silicon for photovoltaic applications is to provide a third "doping" phase of the purified silicon, by elements furthering the photovoltaic power of polysilicon by the passivating of defects, for example, hydrogen.

According to the present invention, once the silicon has been purified, a dopant is introduced into the plasma as a reactive gas, for example, hydrogen. To improve the inclusion of hydrogen atoms in the silicon, the turbulent stirring motions are preferably inverted in the liquid melt. For this purpose, according to the present invention, magnetic yoke 3, which has a ring shape crossed by the plasma at its center, is positioned. Although it is possible to use a ring-shaped magnetic yoke in the form of a coil controlled by an A.C. drive, it will be preferred according to the present invention to use a magnetic yoke formed of a permanent magnet, for example, in the form of two half-rings brought around plasma flame f when the direction of the turbulent stirring is desired to be inverted in the melt. Since this inversion of the turbulent stirring direction by the plasma results, as illustrated in Fig. 2, in driving the liquid to the bottom of the crucible by descending

along the axis and having it rise back up to the free surface along the crucible wall, it furthers the inclusion of hydrogen atoms in the melt.

Preferably, to avoid for the stirring inversion to cause a return to the center of the melt of the gangues and slag rejected at the periphery during the preceding phase, the heating power of crucible 1 is first decreased, to increase the thickness of the solid external layer of the melt, and thus congeal the solid species containing impurities.

In a fourth phase, once the refined and doped silicon is ready, it is cast in the form of ingots adapted to being sawn to obtain solar cells. This casting may, according to an embodiment not shown, be obtained by tilting of the crucible.

According to the embodiment shown in Figs. 1 and 2, the casting is obtained by operating an electromagnetic valve 5 for closing an aperture 14 at the bottom of crucible 1.

For example, an electromagnetic valve may be used with the purpose of melting down a solid silicon plug that obturates the bottom of the crucible. This plug is maintained, during the other phases, in the solid state by cooling down of the wall of aperture 14. A coil 51 surrounding the output aperture is then used. Coil 51 is imbricated in the low portion of the crucible with coil 12 of the actual crucible. The frequency of the current supplying valve coil 51 by means of a generator 52 is adapted to the size of aperture 14 and is thus much higher than the frequency of the current supplying coil 12 of the crucible. Too high a coupling between the two coils is thus avoided. In the covering area of coils 12 and 51, none of these two frequencies is, of course, optimal. In the absence of a current in coil 51, the crucible material at this height is warm, and thus conductive, but solid. When a current is applied to coil 51 of valve 5, the additional heating causes the melting down of this area. This melting progressively propagates downwards, thus opening the valve by melting of the solid silicon plug. The closing of the valve is obtained by cutting off the current in coil 51.

As an alternative embodiment, a small inductive plasma torch placed under the crucible emptying aperture may be used. This torch is then removed at the time when the coupling temperature is reached (this coupling temperature is, in the case of silicon, smaller than the melting temperature).

To process a next load (or batch) of silicon to be refined, a liquid quantity of the preceding phase is preferably left to remain, to avoid a new first starting phase.

It should be noted that the inversion of the stirring direction provided in the third doping phase may also preferentially be provided in the initial starting phase, to improve the mixing of the silicon powders and chips to be melted down by driving them to the center of the crucible and avoiding an immediate trapping by the cold walls.

An advantage of the present invention is that by means of a single installation, coupling an inductive plasma and a cold inductive crucible, a refining of the silicon with respect to all its impurities is obtained. Accordingly, this refining can be obtained in advantageous economical conditions.

Another advantage of the present invention is that it maintains, during purification and doping phases, the silicon in a liquid state by means of a non-contaminating inductive heating means. This heating means is external to the crucible and leaves the melt surface completely free.

Another advantage of the use of a cold inductive crucible is that the liquid silicon is stirred with a high turbulence intensity that furthers matter transfers in the melt. The turbulence induced in the vicinity of the interface accelerates matter transfers between the two phases above and under the free surface and increases reactional kinetics.

Another advantage of the present invention is that the use of a magnetic yoke between the torch and the crucible makes an inversion of the stirring direction possible and, accordingly, the melting of a new silicon load can be furthered and/or the purification can be improved and/or the doping of a refined silicon can be improved.

Of course, the present invention is likely to have various alterations, modifications and improvements which will readily occur to those skilled in the art. In particular, the gases used in the plasma will be chosen according to the impurities to be eliminated from the melt. Further, the practical making of a refining installation enabling implementation of the method of the present invention is within the abilities of those skilled in the art based on the functional indications given hereabove. It will be ascertained to respect the coupling between the plasma and the cold crucible that enables the seeding, without any contamination, of the melting by induction of a semiconductor material, and the use of a ring-shaped magnetic yoke enabling forcing the convection direction in the melt.